Applied Integrated Computational Materials Engineering (ICME) for New Propulsion Materials   (PM057)

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Oak Ridge National Laboratory

2015 DOE Vehicle Technologies Office
Annual Merit Review
2015 June 8-12
Arlington, Virginia, USA

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Overall project *objectives* and *relevance*

Address materials-related technical barriers by applying ORNL's expertise in ICME, materials and powertrain technologies

- **Develop and evolve new capabilities**
  - Develop and apply ***innovative tools and strategies*** **(ICME)** that maximize benefits of predictive information from simulation and experiments

- **Reduce time to market**
  - Enable accelerated application of materials for advanced engine and powertrain systems to meet fuel-economy and emissions goals
  - Facilitate systematic optimization of the design process, integrating energy conversion processes and materials

- **Project supports multiple, multi-year efforts that include industry and university partners**
  - Addresses specific technology barriers identified by DOE and industry stakeholders
  - DOE funds support open, pre-competitive efforts
  - Tools and approaches developed are available to industry for proprietary efforts

- **Project applies ICME approaches to discovery or development of advanced powertrain materials**
  - Identify practical solutions that reduce petroleum dependence by developing enabling materials
  - Apply ICME methods to accelerate development of a diverse group of propulsion materials needs

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ICME accelerates materials development

Public Interface

Designer Interface

Product Development Knowledge Base

Knowledge & Rule Bases

Database

Uncertainty Methods

Use Cases

Cost Models

Manufacturing Process-Material Structure Models

Material Structure Property Models
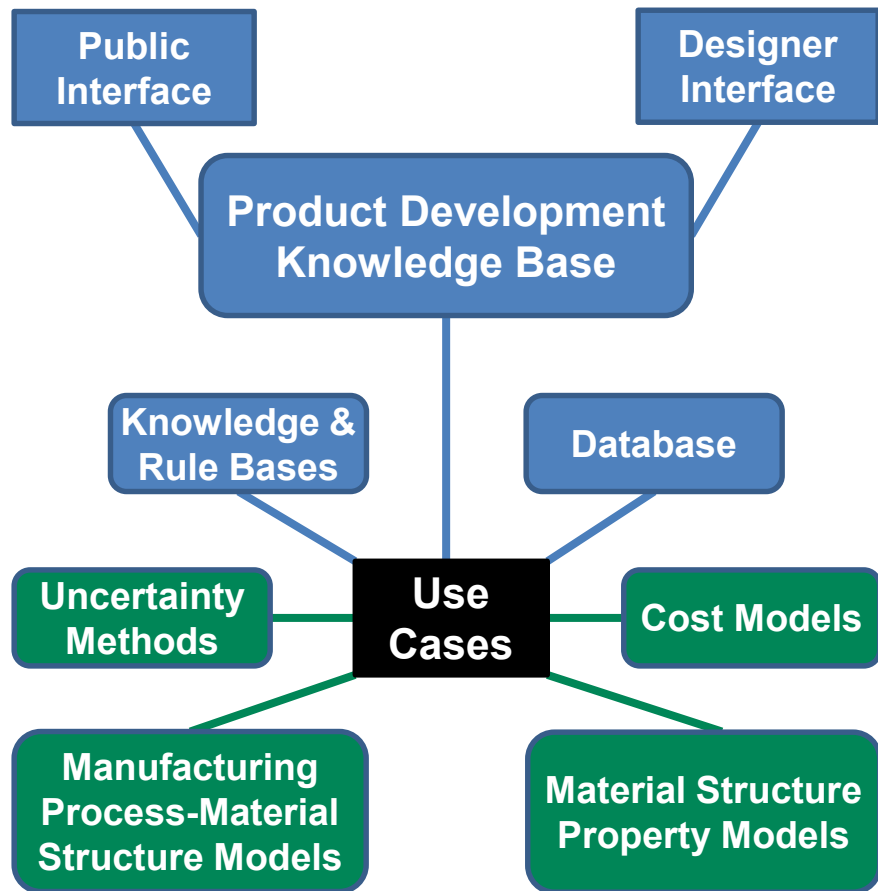
Schematic structure of an ICME system, after *Fig. 1-1 in "Integrated Computational Materials Engineering", NAS Press (2008).*

- Driver (Barrier): Materials development enables new technologies, but is **slow** (15-20 years typical deployment) and **expensive** – need more efficient approaches (Materials Genome Initiative, OSTP).

- Depends strongly on materials type and application.

- Synergy and tighter coupling between activities (modeling & experimental validation) is key.

- Make materials development ***Faster**, **Cheaper**, and **Less Risky***.

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Project Overview

Timeline

- **Project start – Q4 FY2013**
- **Project end – Q4 FY2016**
- **Complete – 60%**

Barriers

- **Directly targets barriers identified in the VTO MYPP**
  - "Changing internal combustion engine combustion regimes"
  - "Long lead times for materials commercialization"
  - "Many advanced vehicle technologies rely on materials with limited domestic supplies"
  - "Need to reduce the weight in advanced technology vehicles"

Budget

- **FY2014 – $825 K**
- **FY2015 – $685 K**
  ($88 K received to date)

Partners

- **John Deere**
- **MIT (S3TEC EFRC)**
- **University of Tennessee**
- **The Ames Laboratory – Critical Materials Institute**
- **Naval Research Laboratory**
- **University of Houston**
- **Caterpillar**
- **Cummins**

Project Organization

Project encompasses 4 tasks applying various Integrated Computational Materials Engineering methodologies.

Applied ICME tasks	FY2015 Budget
1. Piezoelectric materials*	$100 K
2. Non rare earth permanent magnets*	$175 K
3. Low temperature catalyst materials*	$160 K
4. Modeling of HD engines	**$250 K**
	$685 K

◄ Focus of today's talk

These sub-tasks were reviewed in the FY2014 AMR

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ICME FY2015 Milestones

| Milestone	Due/Status
(Piezoelectrics) Identification of a practical oxide composition with a morphotropic phase boundary that has a larger lattice distortion than PZT as measured by the tetragonal c/a ratio on the tetragonal side of the boundary.	Q1 – Completed
(Catalyst Materials) Engine testing of heterobimetallic zeolite catalysts.	Q1 – Moved to Q4 due to delay in funds
(Permanent Magnets) Identify one new rare earth-free ferromagnetic material composed of elements relevant for electric drive systems, and determine its potential for permanent magnet motor applications.	Q1 – Completed
(HD Engine Modeling) Procure advanced cast iron materials for high temperature materials properties measurements.	Q2 – Completed
(Magnetic Materials) Determine effects of alloying the heavy transition metals Mo and W into the most promising Fe5PB-2 type material, including effects on magnetization, Curie temperature and magnetic anisotropy.	Q3 – On track
(Piezoelectrics) Complete calculations for new composition based on PZT showing enhanced ferroelectricity and a morphotropic phase boundary.	Q4 – On track
(HD Engine Modeling) Complete tuning of model to predict physical conditions for current baseline, intermediate stretch and projected future operating conditions	Q4 – On track

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ONGOING TASKS

FY2015 Technical Accomplishments for previously reviewed tasks

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1. Piezoelectric materials for high performance fuel injector actuator applications (single slide summary)

PI: David S. Parker

Motivation: New high performance engines require precise fuel control to meet fuel efficiency standards. Current PZT-based piezoelectric fuel injector actuators are not sufficient for this purpose, necessitating a search for alternatives.

Objective: Discover a piezoelectric compound that exhibits potentially higher performance than PZT, as measured by the atomic displacements on the tetragonal side of the phase boundary.

Impact Result: Found theoretically that $(PZT)_{0.75}(Bi(ZnTi)_{0.5}O_3)_{0.25}$ (left) has much higher A-site (Pb,Bi) displacements than PZT (right), suggesting a likelihood of higher ferroelectric polarization and enhanced piezoelectric response.
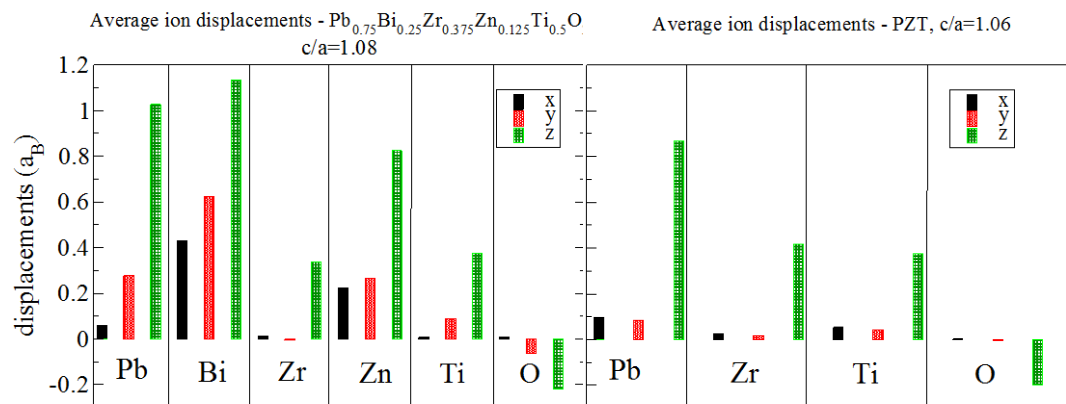
Displacements of atoms from symmetric positions for $(PZT)_{0.75}(Bi(ZnTi)_{0.5}O_3)_{0.25}$ (left) and PZT.

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2. Permanent magnets
(single slide summary)

PI: Michael A. McGuire

Motivation: Rare earth permanent magnets (PM) constitute approximately 30% of current electric drive motor cost. Because of price and supply chain uncertainty, rare earth elements present a substantial barrier to meeting motor cost targets.

Objective: Examine new PM systems and gain better understanding of alternative materials to guide rare earth free PM development.

Impact Result: Identified atomic vibrations in rare earth free PM material MnBi that are coupled to promising high temperature magnetic behavior.
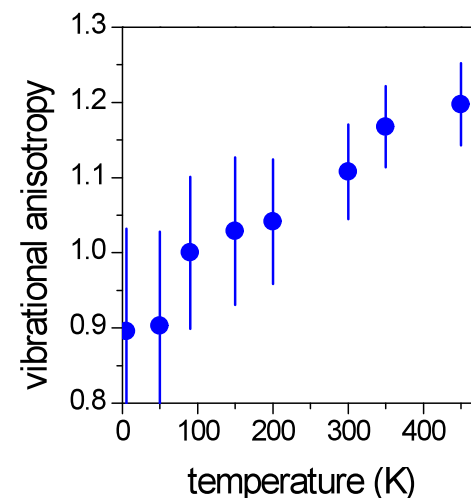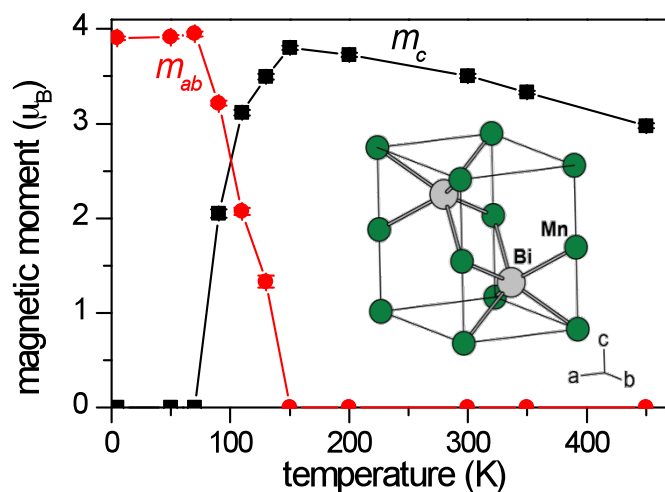
Magnetic moment determined from neutron diffraction showing reorientation from ab-plane to c-axis with higher T, and associated anisotropy of Bi atomic vibrations.

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3. Low-temperature catalysts
**(single slide summary)**

PI: Chaitanya K. Narula

Motivation: Improvements in combustion strategies are resulting in lower exhaust temperatures, necessitating catalysts that can treat exhaust at lower temperatures than currently possible.

Objective: Optimal design of low-temperature performance, and durability of supported catalysts employed in emission treatment; e.g., lean NOx catalyst, three-way catalysts oxidation catalysts, and lean NOx traps etc

Impact Results:

• Found theoretically and experimentally that single supported Pt is an excellent NO oxidation catalyst while single supported Pd is ineffective.

• Employing CuMn-ZSM-5, determined that ion-exchange is superior to impregnation for synthesis of heterometallic zeolites for low-temperature NOx SCR.

• Synthesis & testing of CuPt-ZSM-5 in progress
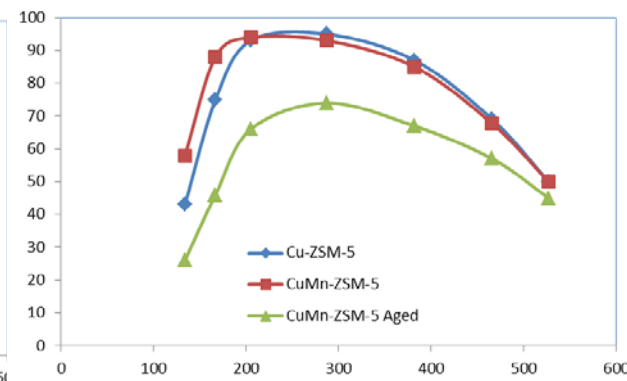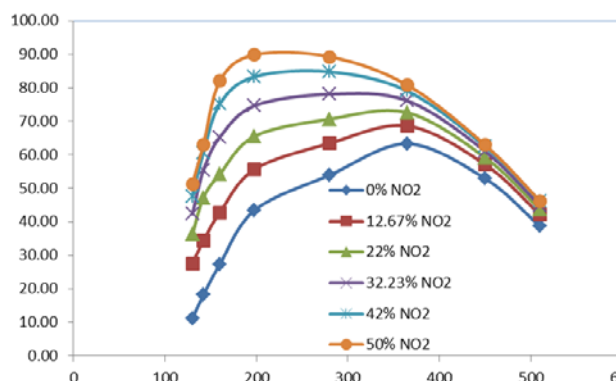
Impact of NO:NO$_2$ ratio (left) and aging (right) on NH$_3$-SCR by CuMn-ZSM-5
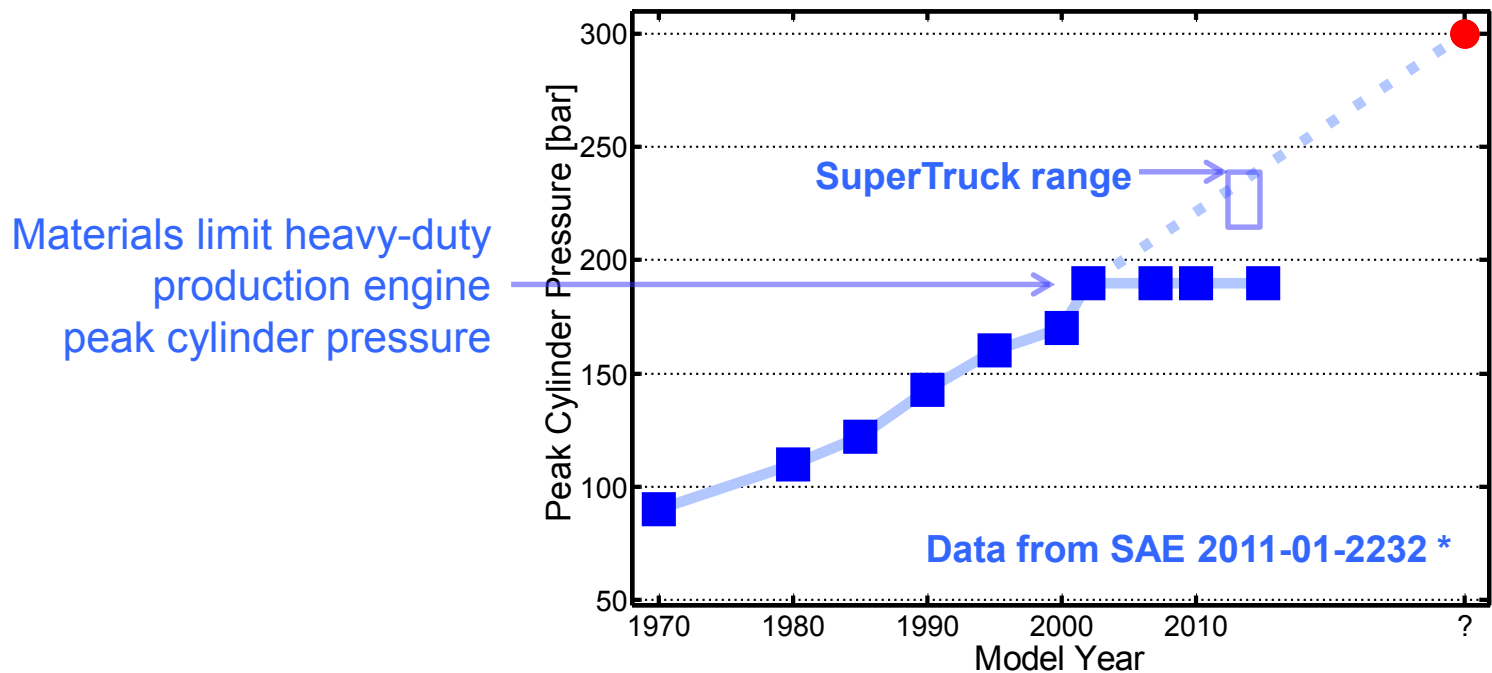
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NEW: TASK 4

Materials needs for next-generation heavy-duty engines at extreme pressures and temperatures

Work began: May 2014

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Tasks and Challenges/Barriers

- Multi-Year Program Plan* Task: Materials for Combustion Systems/High Efficiency Engines
  - Evaluate and characterize emerging materials for application in advanced high-efficiency heavy truck engines

- Challenges/Barriers addressed:
  - "Changing internal combustion engine combustion regimes" – Higher efficiency will require higher pressures and temperatures which will exceed current materials limits.
  - "Long lead times for materials commercialization" – Define future properties requirements to guide development of new materials.
  - "Need to reduce the weight in advanced technology vehicles" – Advanced materials enable higher power densities and more efficient engine designs with lower mass.

* Vehicle Technologies Program Multi-Year Program Plan (2011-2015).
http://www1.eere.energy.gov/vehiclesandfuels/pdfs/program/vt_mypp_2011-2015.pdf

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Enabling high-efficiency engines

- Roadmap for heavy-duty engine operation projects increasingly **higher peak cylinder pressures** (PCP) and **temperatures** into the foreseeable future to meet efficiency targets
  - SuperTruck programs demonstrated >50% BTE with ≈225 bar PCP, for limited operating spans.
  - 300 bar PCP is goal.

Materials limit heavy-duty production engine peak cylinder pressure

SuperTruck range

Data from SAE 2011-01-2232 *

* M. Megel *et al*. SAE 2011-01-2232; *SAE Int. J. Engines* **4**(3).

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Enabling high-efficiency engines

- Current materials are inadequate for these severe conditions
  - Gray Cast Iron and Compacted Graphite Iron have lower strengths than needed.
  - Materials properties typically **degrade with temperature**, compounding the problem.

- Fatigue life is a concern.
- Significant cost restraints.

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Objectives and Approach
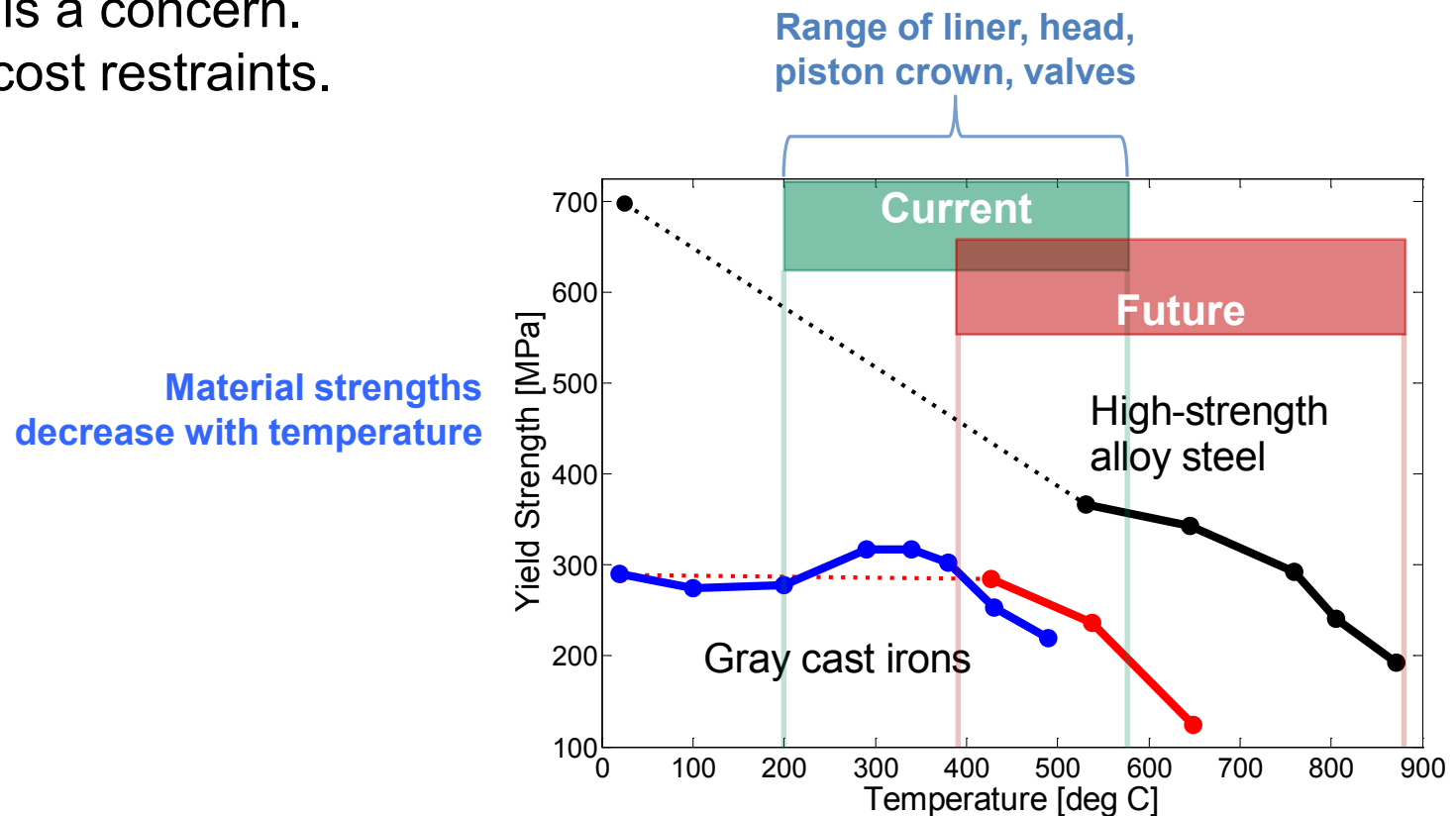
Objectives

- Identify strength and fatigue requirements for current engine-cylinder materials operating at elevated peak cylinder pressures (PCP) and temperatures.

- Define materials properties required to meet lifetime requirements of commercial heavy-duty engines at future extreme operating conditions.

Approach

- Use combustion Computational Fluid Dynamics (CFD) modeling to estimate the thermal environment (temperatures and heat fluxes) at current and future PCP operating points.

- Use Finite Element Modeling to evaluate effects of pressure and thermal environment on engine cylinder components of interest: **head**, **valves**, **liner.**

  - Initial work (FY14): Focus on yield strengths as limit of current materials (Gray Cast Iron); combustion met PCP but loads were not matched in first-phase work

  - Ongoing work (FY15): Focus on fatigue analysis and factors of safety on advanced (Compacted Graphite Iron – CGI) and future engine materials

This task extends boundaries of ICME by coupling with CFD.

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Modeling Approach

- Approach is relevant to modern engines and uses established simulation environments

  - Engine: 2013 15-L 6-cylinder engine; focus on single interior cylinder, up to centerlines of neighboring cylinders

  - Boundary conditions defined by known operating conditions/constraints

  - Interfacing industry-standard packages such CONVERGE™ (CFD), ANSYS® (FEM), and fe-safe® along with custom-developed analysis tools to develop an expanded capability to predict materials requirements
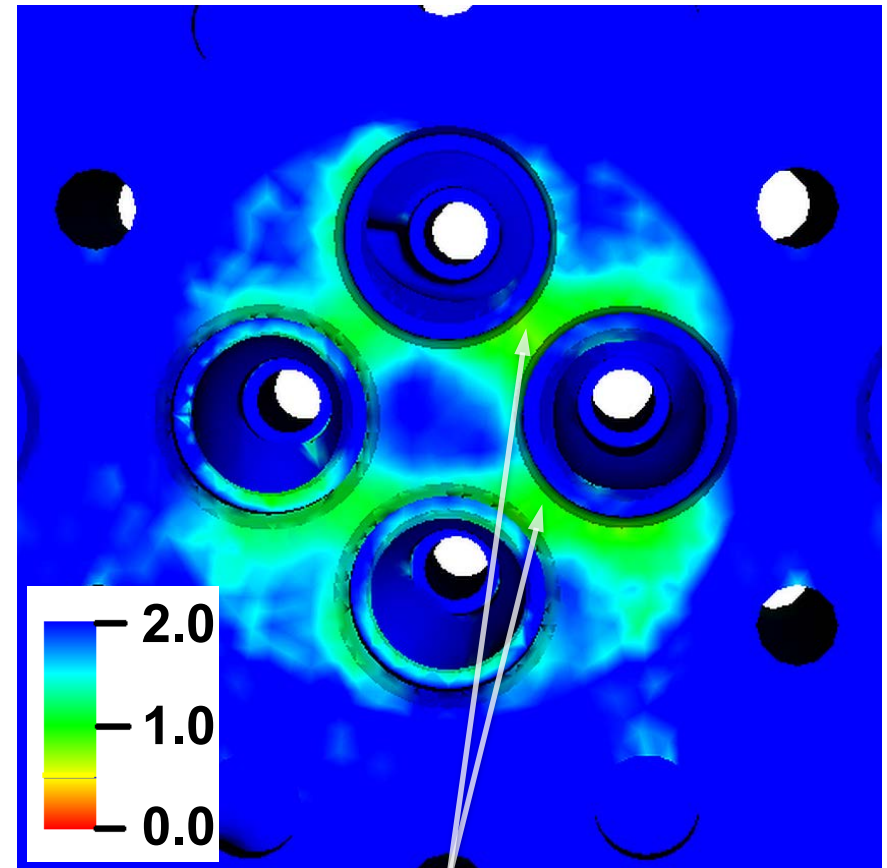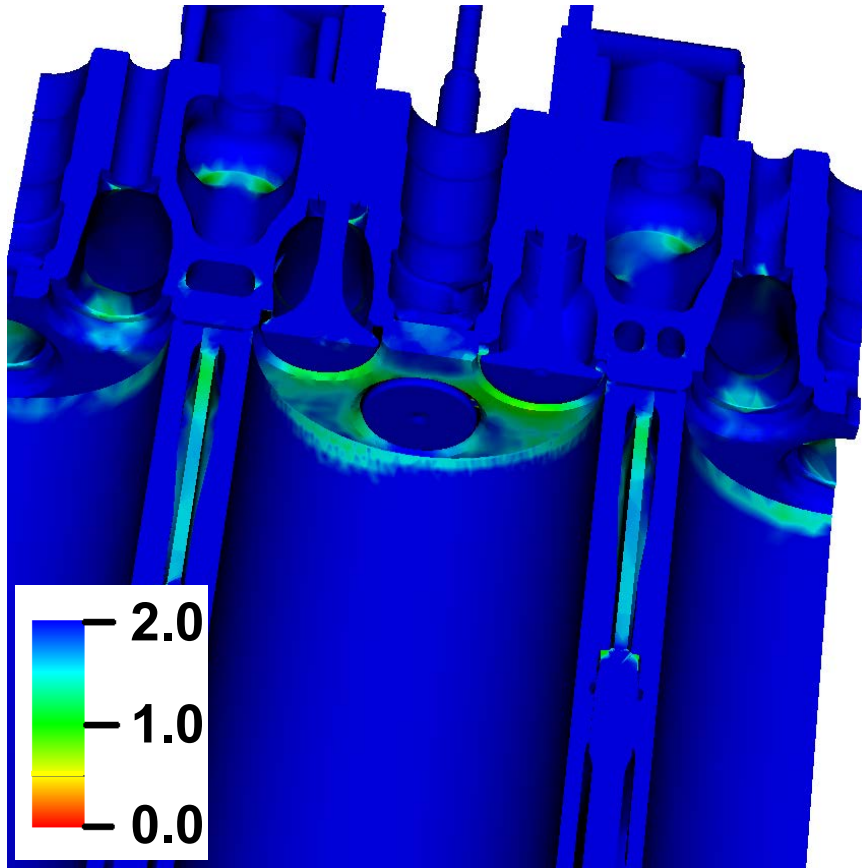
CFD model domain
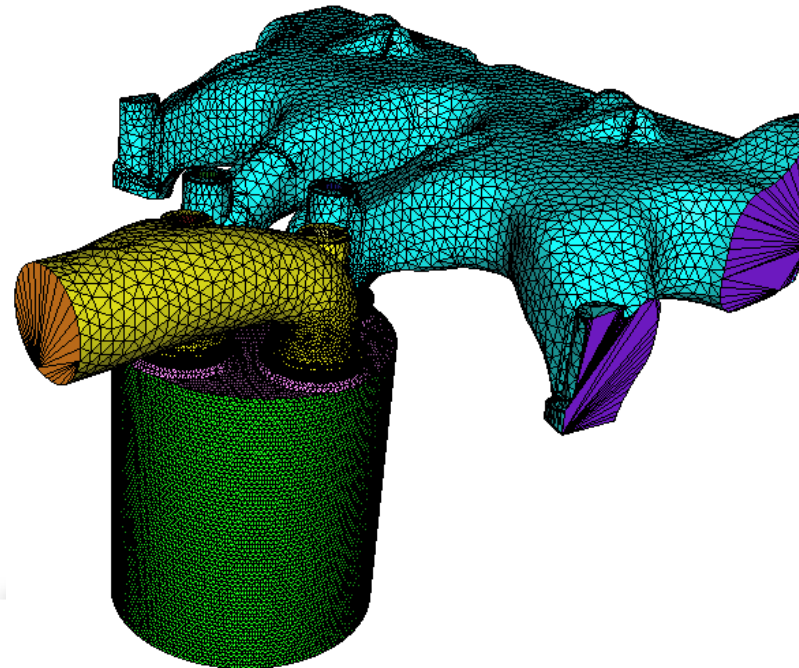
FE model domain
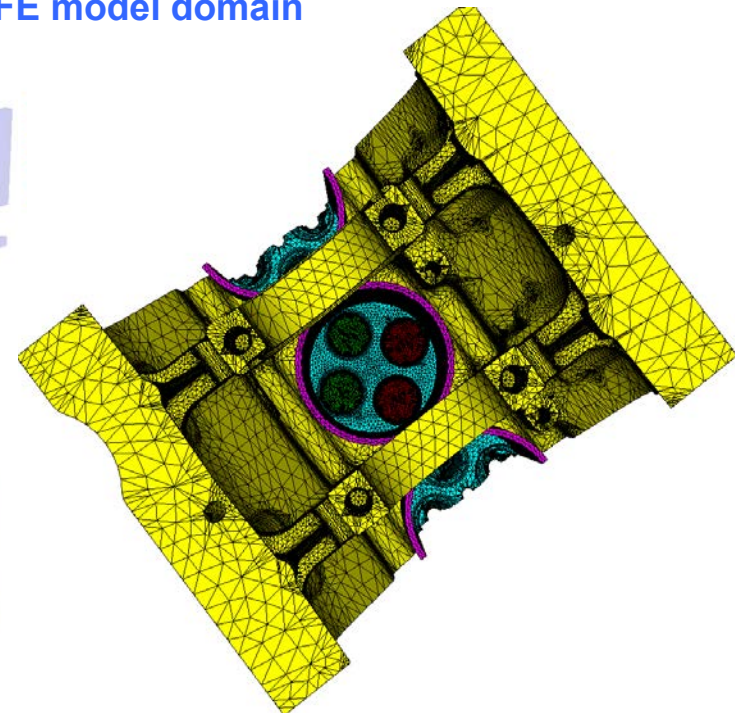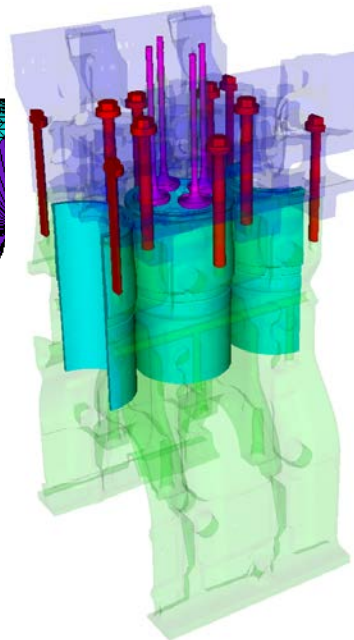
Baselined materials performance at current peak combustion conditions

Safety factors for 190 bar peak cylinder pressure with current materials.

Bridge in head between exhaust valves is concern

Current materials highly stressed but capable at current conditions in production engines. Question: What are the challenges at 300 bar operation?

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Identified materials limitations at future conditions
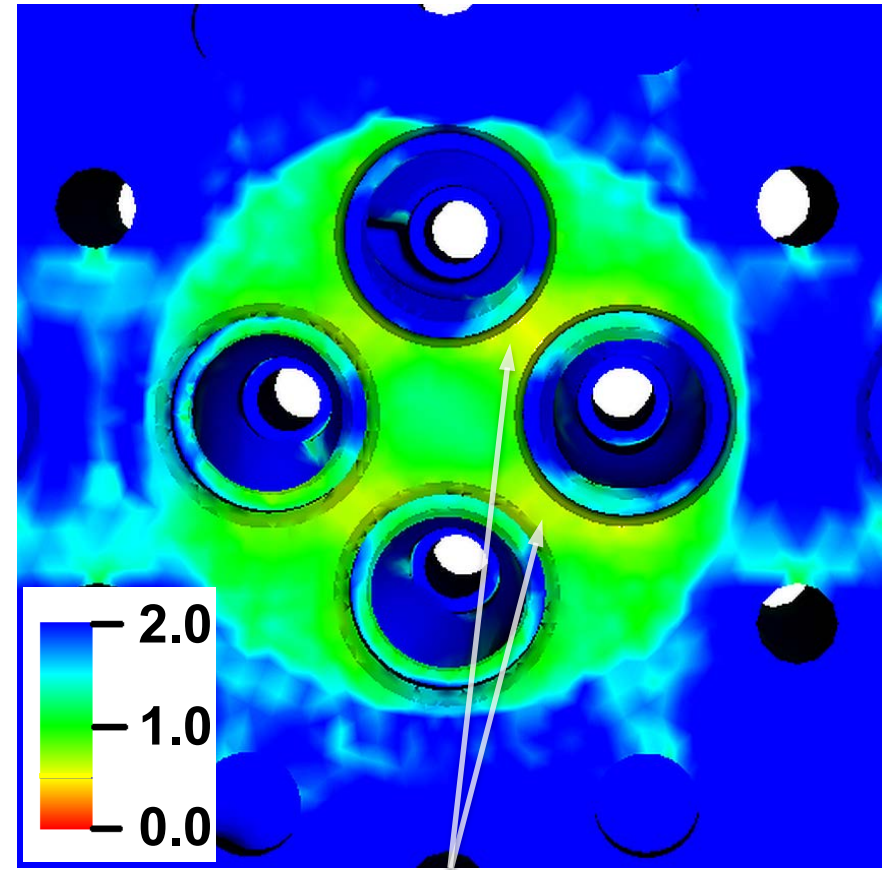
Safety factors for <u>300 bar</u> peak cylinder pressure with current materials.
CFD suggests heat flux > 150% over 190-bar condition.
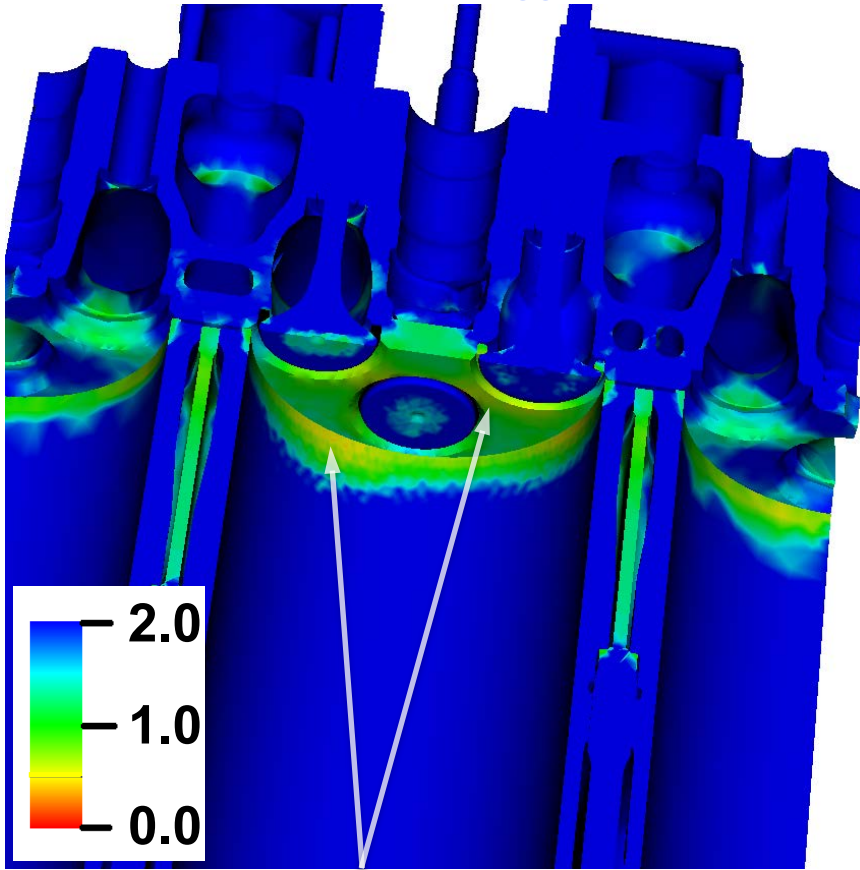
Liner & head severely stressed at 300 bar PCP

Head between exhaust valves will exceed yield strength

This a conservative evaluation – with injector in place, head stresses would be much higher.

Initial focus was on yield stress. Ongoing work will also include fatigue.

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Activities and Progress in FY2015

Materials characterization   (underway)

– Experimentally measure relevant properties for CGI-450 at a range of temperatures
- Tensile strength
- Thermal diffusivity   [partially complete]
- Coefficient of thermal expansion   [partially complete]
- Critical temperatures   [partially complete]
- Specific heats   [partially complete]
- Short-term creep

Gap: No publicly available CGI-450 property data at elevated temperatures relevant to future engine operation. Materials property data from this study will be published.

Combustion modeling   (underway)

– Tune model for three PCP conditions: **190** (current practice), **225** (SuperTruck range), **300** bar.
– Define thermal environment for FEM, and estimate indicated efficiencies.

FEM   (pending)

– Repeat current materials (Gray Cast Iron) at tuned combustion conditions, evaluate Compacted Graphite Iron with newly measured temperature-dependent properties.
– Define required materials properties to meet performance requirements at 225 and 300 bar PCP.
– Focus on fatigue life and safety factors.

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Future research

- Implement fully coupled CFD-FEM tools to improve accuracy and flexibility of simulations.

  ➔ Non-trivial problem – most fully coupled simulations have operated on single small components (e.g., exhaust manifold, turbocharger assembly)

- Refine estimates of future materials properties needed to achieve operating life of production heavy-duty engine at very high temperatures and pressures.

- Stretch: Extend methodology to light-duty engines – higher-temperature but lower service life environment with lower cost margins.

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Responses to Prior Year Comments

- **Reviewer comments: One reviewer commented that bundling all four tasks together under ICME overlooked their individual advances and successes, and that combining four separate applications into one ICME project made it difficult to combine into a coherent story.**

  – We agree that it is challenging to create a coherent story when linking all of the various approaches into one combined multi-task project. However, that challenge is also reflective of the diversity of ICME approaches, philosophies and range of effectiveness at the present time. These are independent tasks, but together they employ and illustrate the diversity of approaches to ICME. The first priority of each task remains to apply these tools to address real materials needs and opportunities. Some tasks seek to modify existing materials, some to predict or discover new materials, some to understand mechanisms, and some to predict the materials properties needed for future materials in future engine designs.

- **Two reviewers stated that the roles of the collaborators were not clearly described.**

  – We agree with this observation and will address it in the future where possible. There are some cases where partners are involved and willing to be acknowledged, but do not want their specific role publicly described. In those cases, we will have to continue to be non-descriptive.

- **One reviewer stated that not enough information on the models employed, critical variables, properties and target performance were provided.**

  – We agree that more of such information would have been an improvement. That is being addressed in the future by rotating reviews of only 1 -2 tasks annually for a more thorough treatment.

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Summary

Contact:
Allen Haynes
haynesja@ornl.gov

Relevance

- Directly addressing materials barriers to enable advanced engine and powertrain systems for propulsion applications

Approach

- Apply ICME methods linking experiments and computational methods to accelerate materials selection and development

- Extend capabilities to address problems using novel approaches

Accomplishments

- Identified alternative non-rare-earth material for permanent magnet applications

- Identified potential new piezoelectric material

- Demonstrated improved material for low-temperature catalysis identified through earlier modeling efforts

- Implemented coupling of CFD and FEM for specifying future materials needs

- Initiated measurement of materials properties of CGI-450 at engine-relevant temperatures
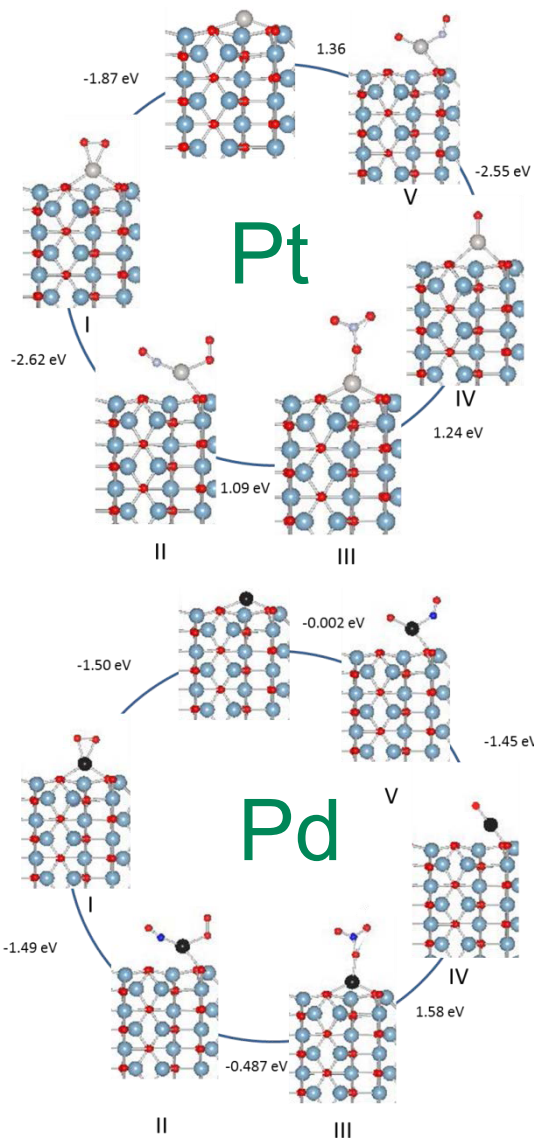
Collaborations

- Collaborations with industry and university partners are producing shared materials and ideas that are relevant to commercial application in next-generation powertrains
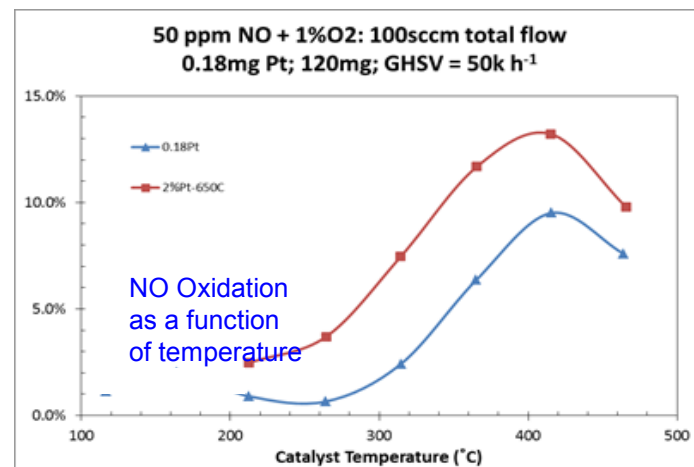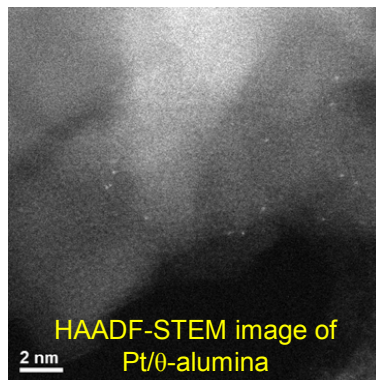
Future work

- Specify materials properties for HD engine operation at 300 bar to meet lifespan needs

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Technical Back-Up Slides

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NO oxidation on single supported atoms

Pt

Pd

Proposed pathways for NO oxidation over single supported Pt and Pd

HAADF-STEM image of Pt/θ-alumina
2 nm

50 ppm NO + 1%O2: 100sccm total flow
0.18mg Pt; 120mg; GHSV = 50k h^{-1}

NO Oxidation as a function of temperature

- Modeling: single supported atoms can be catalytically active [1] → Synthesis / Characterization of mono-disperse single atoms on θ-alumina confirms for CO oxidation [2].

- Recent results: NO oxidation occurs on single supported Pt but requires high temperatures; more efficient on large particles – mechanism?

- Mechanistic studies suggest (a) no nitrate on Pt (b) nitrate on Pd at low temperature
  – DRIFTS should validate the mechanism

[1] Narula et al., J. Phys. Chem. **116**, 5628 (2012). [2] Narula et al., JACS **135**, 12634 (2013).

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Requirements for good permanent magnets

<u>Parameters characterizing magnetic performance:</u>

- Curie temperature (T_C)
- Remanent magnetization (M_r), induction (B_r)
- Coercive field (H_c)
- **Energy product (BH)**

Magnetic hysteresis loop
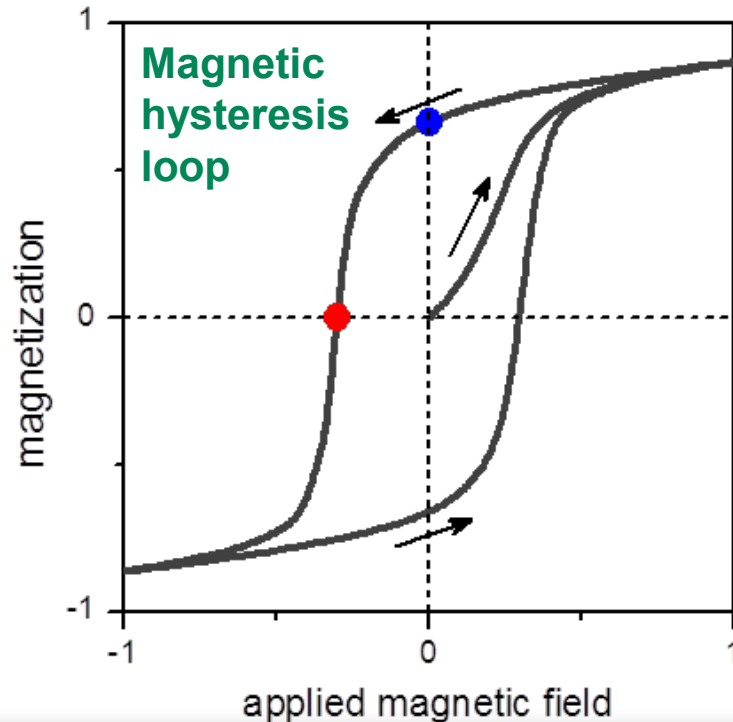
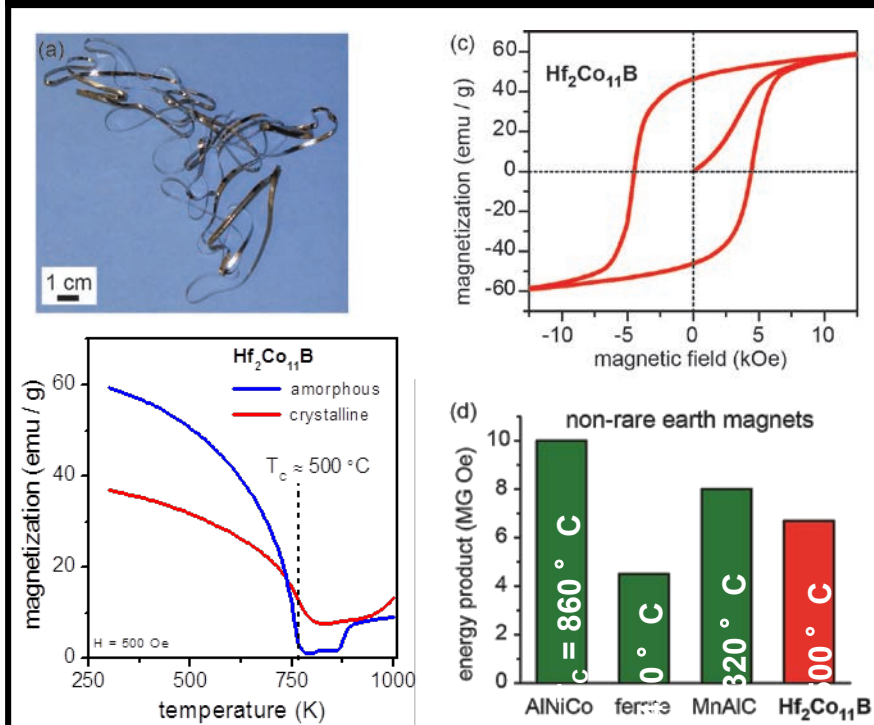

<u>Material Requirements:</u>

- **Large magnetic moments:** iron, cobalt (manganese, chromium)

- **One direction for magnetization:** non-cubic crystal structures

- **Co-alignment of magnetic particles:** highly textured microstructure

- **Strong resistance to switching magnetization direction (hard):** *magnetocrystalline anisotropy*, small particles, refined microstructures

- **High Curie temperature**: strong magnetic interactions

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Hf$_2$Co$_{11}$B alloys

- **In previous project:** Identified (Zr/Hf)$_2$ Co$_{11}$ as promising material for study.
- Modified composition with B and produced hard magnetic material directly via melt spinning.

**Patent Application Filed Oct. 2013**

Key Findings:

- **Demonstrated BH$_{max}$ = 6.7 MGOe**
- Energy product competitive with well-established, long-studied non-rare earth magnet materials.
- Energy product near half that obtained in optimized NdFeB melt-spun ribbons.
- Curie temperature ~150° C higher than NdFeB.
- *Analysis suggest at least a factor of two increase in energy product possible*.

Hf$_2$Co$_{11}$B: melt-spun ribbons and magnetic properties

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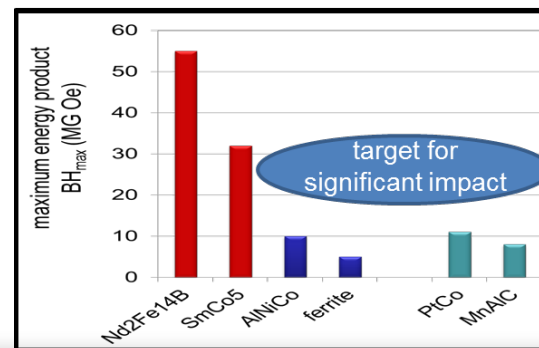
Development of hard magnetism by thermal treatment of amorphous $Hf_2Co_{11}B$

Goal: Develop hard magnetic behavior via annealing of amorphous precursor, and obtain information about the hard magnetic

500 °C, 28 h — 1 µm

annealing

500 °C, 1 h — 1 µm
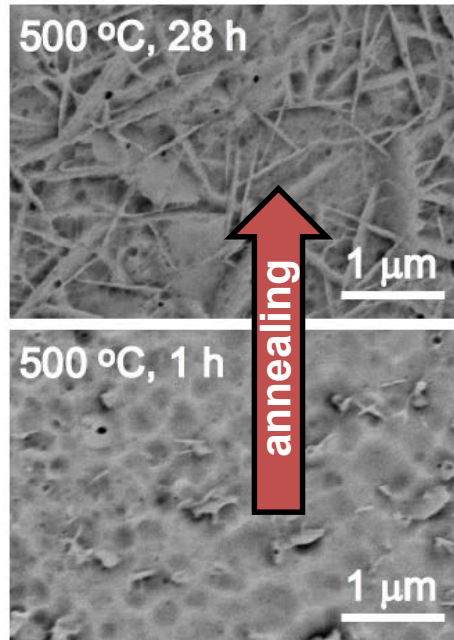
- Extensive annealing study.

- Focus on microstructural evolution and development of magnetic properties.

- **Multiphase materials**

- Best properties obtained by processing far from equilibrium.

- Hard phase forms elongated precipitates.

- Coexistence with magnetically soft matrix gives best properties.

- Morphological identification of the hard phase enables *study of crystal structure and composition*.

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